

# PATENT SPECIFICATION

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## (54) IMPROVED PROCESS FOR PRODUCING AROMATIC SECONDARY (C<sub>3</sub>—C<sub>7</sub> ALKYL) HYDROPEROXIDES

(71) We, HERCULES INCORPORATED, a corporation organized under the laws of the State of Delaware, one of the United States of America, of 910 Market Street, City of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is in the chemical arts. In particular it is in that art pertaining to oxidation processes.

In a well-known process for producing phenol and acetone, cumene is oxidized with molecular oxygen to cumene hydroperoxide which is reacted with sulfuric acid of the like to form phenol and acetone. The oxidation generally is carried out by admixing cumene in the liquid state with an oxygen-bearing gas such as air, oxygen, or mixtures of oxygen and one or more inert gases, and preferably an aqueous solution of a base (for example, an alkali such as sodium carbonate, sodium hydroxide, or the like). The oxidation reaction generally is performed in stages in at least two and generally three or four reactors usually positioned at the same level with the base solution generally being introduced into each of the reactors. Cumene is introduced into an initial oxidation reactor and reaction mixture or oxidate from the initial reactor is introduced into another oxidation reactor. When a third reactor is employed, reaction mixture or oxidate from the preceding or intermediate oxidation reactor is introduced into the third or final oxidation reactor. When a fourth reactor is used, reaction mixture or oxidate from the first intermediate reactor is introduced into the second intermediate reactor and reaction mixture or oxidate from the second intermediate reactor is introduced into the final oxidation reactor. Generally fresh oxygen-bearing gas is introduced into each of the reaction mixtures in the reactors. The rate of flow of the gas into each of the reactors is usually in substantial excess of the rate at

which all the oxygen is consumed by the reaction in each reactor. One reason is to assure a maximum rate of oxidation. Another reason is to obtain the desired degree of mixing of the reactants in the reactors. Gas reaching the top of each of the reactors is removed as off-gas, treated to recover unreacted vaporized cumene, and then disposed of. In the three-reactor or three stage process the cumene hydroperoxide concentration of the initial reactor oxidate is about 6—10% by weight, of the intermediate reactor oxidate is about 13—17% by weight, and of the final reactor oxidate is about 20—30% by weight.

This general stage-wise oxidation procedure is employed in the production of other phenols and ketones from secondary (C<sub>3</sub>—C<sub>7</sub> alkyl) aromatic hydrocarbons such as, for example, m- and p-cymenes; α- and β-isopropyl-naphthalenes; m- and p-diisopropylbenzenes; 2-butylbenzene; 2-pentylbenzene, and the like. The phenols corresponding to the m- and p-cymenes are m- and p-cresols. The phenols obtained from α- and β-isopropyl-naphthalenes are α-naphthol and β-naphthol. The phenols derived from m- and p-diisopropylbenzene are m- and p-isopropylphenol, resorcinol and hydroquinone. 2-Butylbenzene and 2-pentylbenzene result in phenol itself. The ketone obtained from 2-butylbenzene is methyl ethyl ketone. The ketone obtained from 2-pentylbenzene is methyl propyl ketone.

This invention in its various embodiments provides improvements of this oxidation process.

These improvements are made possible by the fact the oxidation by molecular oxygen of secondary C<sub>3</sub>—C<sub>7</sub> alkyl substituted aromatic hydrocarbons in the liquid state is in each case a zero order reaction. In other words, above a certain minimum concentration of molecular oxygen, the rate of oxidation is independent of the quantity of molecular oxygen present.

Hence, when an excess of oxygen-bearing gas is passed through each reaction mixture

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in the prior process, the off-gas contains a substantial quantity of unreacted molecular oxygen.

5 In summary, according to this invention, in which the reactors are broadly considered as oxidation zones, at least part of the off-gas from a succeeding or a second oxidation zone is used as at least part of the oxygen-bearing gas passed through the reaction mixture in the immediately preceding or first oxidation zone.

10 Hence, in a three-stage embodiment of this invention at least part of the intermediate oxidation zone off-gas is employed as at least part of the oxygen-bearing gas passed through the reaction mixture in the initial oxidation zone, and preferably, at least part of the final oxidation zone off-gas is employed as at least part of the oxygen-bearing gas passed through the reaction mixture in the intermediate oxidation zone. Preferably the hydroperoxide concentration in the initial oxidation zone oxidate is 6 to 10% by weight, the hydroperoxide concentration in the intermediate oxidation zone oxidate is 13 to 17% by weight, and the concentration of the hydroperoxide in the final oxidation zone oxidate is 20 to 30% by weight.

25 Another concept involved in preferred embodiments of this invention comprises a preceding or a first oxidation zone being above a succeeding or a second oxidation zone so that reaction mixture from the first zone flows downwardly into the second zone, and at least part of the second zone off-gas flows upwardly into the reaction mixture in the first zone.

30 Hence, in a preferred three-stage embodiment of this invention, the initial zone is above the intermediate zone, the intermediate zone is above the final zone, at least part of the final zone off-gas is introduced into the reaction mixture in the intermediate zone, at least part of the intermediate zone off-gas is introduced into the reaction mixture in the initial zone, reaction mixture from the initial zone is introduced into the intermediate zone, and reaction mixture from the intermediate zone is introduced into the final zone.

40 In a preferred three-stage embodiment of the process of this invention, the three oxidation zones are formed by a vertically disposed column of tower horizontally divided by vertically spaced gas permeable means into three superposed compartments. Means are provided for introducing a secondary  $C_3-C_7$  alkyl substituted aromatic hydrocarbon feed into the top compartment, for introducing aqueous base solution into at least the top compartment, for introducing oxygen-bearing gas into the bottom region of at least the bottom compartment, for withdrawing oxidate from the top compartment and introducing it into the middle compartment, for withdrawing oxidate from the middle compartment and introducing it into the bottom compartment, for withdrawing product oxidate from the

bottom compartment, and for withdrawing off-gas that reaches the top of the top compartment.

70 In the practice of the various embodiments of the process of this invention the prior art conditions of temperature and pressure are generally employed, and the aqueous base solution is any one of the aqueous solutions of bases suggested or used in the prior art. Thus, reaction temperatures in the range from about 90 to about 130° C. and preferably from about 90 to about 115° C. are used. However, higher and lower temperatures are within the broader concepts of this invention. Reaction pressures in the range from about 30—120 pounds per square inch gauge are used, but higher and lower pressures are within the broader concepts of this invention. The aqueous solution of base is composed of water and a base which is relatively inert to the hydrocarbon and the hydroperoxide. Examples of such material include alkalis such as alkali metal hydroxides, alkali metal carbonates, and the like, amines, ammonia, and the like. The flow rate of the aqueous base solution introduced into each oxidation zone is selected to establish and maintain the reaction mixture at a pH of about 5—8, but higher and lower pHs are within the broader concepts of this invention.

95 The best mode now contemplated of carrying out this invention is illustrated by the drawing which forms a material part of these disclosures, and which illustrates diagrammatically a flow sheet for carrying out a preferred specific embodiment of the process of this invention.

100 More particularly, the drawing displays a flow sheet in which a vertically disposed tower or column 10 is diagrammatically shown. The column 10, formed by a cylindrical casing with a top 12 and a bottom 14, is divided internally by two horizontally disposed vertically spaced trays 16 and 18 into superposed compartments 20, 22 and 24 which function as oxidation zones. In the embodiment of the column 10 shown in the drawing each of the two trays 16 and 18 is provided with at least one opening 26 in combination with an upriser 28 and a bubble cap 30 for delivering gas from below the tray into the compartment and bubbling it into the liquid that collects on the tray. Generally each tray has a plurality of such openings uniformly spaced with uprisers 28 and bubble caps 30.

120 In another embodiment of the column 10 each of the trays 16 and 18 is a sieve plate which is perforated sufficiently to prevent passage therethrough of gas from the compartment below.

125 In still another embodiment of the column 10 each of the trays 16 and 18 is a sinuous or ripple-like sieve plate which is perforated sufficiently to prevent the downflow of liquid that collects on the plate, while permitting

the upflow of gas from the compartment below.

In the embodiment shown, the top compartment 20 has a discharge outlet in the region of its bottom formed by upper tray 16, to which is joined an initial reaction mixture withdrawal conduit 32 provided with a flow control valve 34. This conduit leads generally downwardly to the feed inlet of the intermediate compartment 22. Similarly, the intermediate compartment 22 has in the region of the bottom thereof formed by the lower tray 18 a discharge outlet to which is connected an intermediate reaction mixture withdrawal conduit 36 provided with a flow control valve 38. This intermediate reaction mixture withdrawal conduit extends generally downwardly to a feed inlet of the bottom compartment 24.

In other embodiments of the column 10, in addition to the first and second reaction mixture withdrawal conduits 32 and 36, the trays have downcomers for conducting reaction mixture to the respective subjacent compartments.

In still other embodiments only downcomers are employed to conduct first and second reaction mixtures to the respective subjacent compartments.

The top compartment has a hydrocarbon feed inlet to which is joined a hydrocarbon feed conduit 40 having a flow control valve 42 and preferably a feed stream-hydroperoxide product heat exchanger 44 and an auxiliary heat exchanger 46.

The bottom compartment 24 is provided with a gas sparger 48 connected to a branch gas conduit 50 provided with a flow control valve 52 joined to the main gas conduit 54. Preferably, the intermediate compartment 22 is provided with a gas sparger 56 joined to a branch gas conduit 58 provided with a flow control valve 60 and also joined to the main gas conduit 54. A main feed conduit 62 for the aqueous solution of a base is provided to which is joined a branch feed conduit 64 (with a flow control valve 66) leading to an inlet in the top compartment 20, a branch feed conduit 68 (with a flow control valve) leading to an inlet in the intermediate compartment 22, and a branch feed conduit 72 (with a flow control valve 74) leading to an inlet in the bottom compartment 24.

The top 12 of the column 10 has a gas outlet connected to an off-gas discharge conduit 76 provided with a flow control valve 78 and a condenser 80. The off-gas discharge conduit terminates at an inlet in a storage tank 82 having a spent gas discharge conduit 84 at the top thereof and at the bottom thereof a condensate withdrawal conduit 86 with a flow control valve 88. The condensate withdrawal conduit is joined to an inlet in the top compartment 20.

At the bottom of the column 10 there is an outlet connected to a hydroperoxide product

discharge conduit 90 with a flow control valve 92 and one element (here depicted as a coil) of the feed stream-hydroperoxide product heat exchanger 44.

Preferably the top compartment 20 is provided with a heating coil 94 and an emergency cooling coil 96 connected to external conduits with flow control valves. Similarly, the intermediate compartment 22 has a heating coil 98, a temperature regulating cooling coil 100 and an emergency coil 102, which are connected to external conduits with flow control valves. Also, the bottom compartment preferably has a heating coil 104, a temperature regulating cooling coil 106 and an emergency cooling coil 108 which are connected to external conduits with flow control valves.

Under normal operative conditions, with an excess of oxygen-bearing gas being introduced by way of the main gas conduit 54 and bottom compartment gas feed conduit 50 into the bottom compartment 24, and preferably with an excess of oxygen being introduced by the intermediate compartment gas feed conduit 58 into the intermediate compartment 22, secondary ( $C_3$ — $C_7$ ) alkyl substituted aromatic hydrocarbon feed is introduced by way of hydrocarbon feed conduit 40 into the top compartment 20. When the desired static level of the liquid content of the top compartment 20 is reached, which usually is near the region of the top of the compartment, the valve 34 in the initial reaction mixture withdrawal conduit 32, which valve can be linked to an automatic level controller (not shown), is opened and initial reaction mixture is withdrawn from the top compartment 20 at a rate at which the desired static level of the liquid content of the top compartment 20 is established and maintained, and introduced into the intermediate compartment 22. Similarly, when the desired static liquid level has been reached in the intermediate compartment, which usually is in the region of the top of the compartment, the valve 38 in the intermediate reaction mixture withdrawal conduit 36, which valve likewise can be linked to an automatic level control in the intermediate compartment, is opened and intermediate reaction mixture is withdrawn from the intermediate compartment 22 at a rate at which the desired static level of the liquid content of the intermediate compartment 22 is established and maintained, and introduced into the bottom compartment 24. When the desired static liquid level is reached in the bottom compartment 24, which usually is in the region of the top of the compartment, the product discharge valve 92 is opened and final reaction mixture is removed by way of the hydroperoxide product discharge conduit 90.

In the meantime, aqueous solution of alkali is passed through the manifold conduit 62 and branch feed conduits 64, 68 and 72 into the

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- top, intermediate and bottom compartments at rates selected to establish and maintain the pH of the reaction mixtures in those compartments in the range from about 5 to about 7. The temperature of the hydrocarbon feed stream is established and maintained within a selected range by means of the feed stream-hydroperoxide product discharge heat exchanger 44 and the auxiliary heat exchanger 46. The selected range depends on the composition of the hydrocarbon and the optimum temperature range for oxidation. In all cases, however, the selected range is less than the boiling point of the hydrocarbon.
- The desired temperature conditions in the top, intermediate and bottom compartments 20, 22 and 24 are established and maintained by the heating coil 94 in the top compartment 20, the heating coil 98 and cooling coil 100 in the intermediate compartment 22, and the cooling coil 104 and heating coil 106 in the bottom compartment 24.
- Off-gas from the column 10 is discharged from the top compartment 20 through the off-gas discharge conduit 76 and passed through a condenser 80. The condensate and spent gas flow from condenser 80 into a hold tank 82. The spent gas is disposed of by spent gas discharge conduit 84, while the condensate, composed of water and secondary ( $C_3-C_7$ ) alkyl substituted aromatic hydrocarbon is removed from the hold tank 82 by way of conduit 86 and returned to the top compartment 20.
- Typical steady state conditions and flow rates in the practice of the process of this invention to produce cumene hydroperoxide from cumene are as follows: —
- The feed consists essentially of cumene. The oxygen-bearing gas is air and the aqueous solution of alkali is a 1% by weight aqueous solution of sodium carbonate. The temperature of the top compartment or initial oxidation zone 20 is established and maintained at about 113°. The temperature of the intermediate compartment or oxidation zone 22 is established and maintained at 105° C. The temperature of the bottom compartment or final oxidation zone 24 is established and maintained at 103° C. Pressure as measured at the top of the column 10 is established and maintained at about 80 psig (pounds per square inch gauge).
- Typical flow rates in pounds per hour are presented in the following table in which the numerals in the column headings identify the conduits in the drawing: —
- |    |  |
|----|--|
| 30 |  |
| 35 |  |
| 40 |  |
| 45 |  |
| 50 |  |
| 55 |  |

Components	Cumene Feed Stream (40)	Aqueous Solution of Alkali			O <sub>2</sub> Bearing Gas		Spent Gas (84)	Hydroperoxide Product (90)
		(64)	(68)	(72)	(50)	(58)		
Oxygen					1,633	817	223	
Nitrogen					5,373	2,687	8,060	
Water		408	408	408	93	47	7	1,400
Cumene	43,253						7	34,753
Cumene Hydroperoxide $\alpha,\alpha$ -Dimethylbenzyl Alcohol								10,000 572
Acetophenone								75
Sodium Carbonate		4	4	4				10
Sodium Bicarbonate								7
Carbon Dioxide								25
Total	43,253	412	412	412	7,099	3,551	8,297	46,842

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A major feature of advantage of the improved process of this invention is that substantially less oxygen-bearing gas is required to obtain the yield of hydroperoxide product obtained by the prior art process. Consequently, the gas compressor for the process can be substantially smaller, the power requirements to compress the oxygen-bearing gas can be reduced significantly, and the components for the off-gas treatment system can be reduced in size.

A feature of advantage of the tower or column embodiment of the process of this invention pertains to cost of construction. The column is less expensive to construct than three or four separate reactors. It is also less expensive to construct a column transversely separated into superposed compartments than to partition a tank into quadrants as in U.S. patent 2,829,173.

Another feature of advantage of the tower or column embodiment of the process of this invention is better agitation of the reaction mixtures. For proper agitation in an oxidation zone the linear velocity of gas passed through the reaction mixture should be above 0.07 foot per second, and preferably above 0.10 foot per second. Because of the large height to diameter ratio inherent in the tower embodiment, better agitation is obtained because the same gas agitates the reaction mixture in alkali oxidation zones rather than in just one oxidation zone as in the prior art process.

Still another feature of advantage of the tower embodiment of the process of this invention is the better utilization of reactor space that is made possible. The disengaging space at the top of the intermediate and bottom compartments can be less than in the case of separate or quadrant type reactors because a small amount of gas entrainment of reaction mixture from these compartments into the compartments above will do no harm.

#### WHAT WE CLAIM IS:—

1. A continuous process for oxidizing a secondary  $C_3$ — $C_7$  alkyl substituted aromatic hydrocarbon to the corresponding aralkyl hydroperoxide, which comprises:—

introducing said hydrocarbon into a first reaction mixture in a first oxidation zone, said first reaction mixture comprising said hydrocarbon in the liquid state, an aqueous solution of alkali, and said hydroperoxide;

withdrawing from said first oxidation zone as first oxidation zone oxidate part of said first reaction mixture;

introducing first oxidation zone oxidate into a second reaction mixture in a second oxidation zone, said second reaction mixture comprising said hydrocarbon in the liquid state, an aqueous solution of alkali, and said hydroperoxide, the concentration of said hydroperoxide in said second reaction mixture being substantially

greater than the concentration of said hydroperoxide in said first reaction mixture;

withdrawing from said second oxidation zone as second oxidation zone oxidate part of said second reaction mixture;

introducing aqueous solution of alkali into at least said first reaction mixture in said first oxidation zone;

admixing with said second reaction mixture in said second oxidation zone oxygen-bearing gas at least at a rate selected to establish and maintain oxygen in said second reaction mixture in stoichiometric excess relative to said hydrocarbon in said second reaction mixture;

withdrawing as second oxidation zone off-gas from the upper portion of the second oxidation zone gas reaching said upper portion;

admixing with said first reaction mixture in said first oxidation zone oxygen-bearing gas at a rate selected to establish and maintain oxygen in said first reaction mixture in stoichiometric excess relative to said hydrocarbon in said first reaction mixture, at least part of said oxygen-bearing gas being second oxidation zone off-gas; and

withdrawing from the upper portion of the first oxidation zone any gas reaching said upper portion.

2. A process according to claim 1 in which said oxygen-bearing gas admixed with said second reaction mixture in said second oxidation zone comprises air.

3. A process according to claim 1 or 2, which comprises:—

introducing second reaction zone oxidate into a third reaction mixture in a third oxidation zone, said third reaction mixture comprising said hydrocarbon in the liquid state, an aqueous solution of alkali, and said hydroperoxide, the concentration of said hydroperoxide in said third reaction mixture in said third oxidation zone being substantially greater than the concentration of said hydroperoxide in said second reaction mixture in said second oxidation zone;

withdrawing from said third oxidation zone as third oxidation zone oxidate part of said third reaction mixture; admixing oxygen-bearing gas with said third reaction mixture in said third oxidation zone at least at a rate selected to establish and maintain oxygen in said third reaction mixture in stoichiometric excess relative to said hydrocarbon in said third reaction mixture;

withdrawing as third oxidation off-gas from the upper portion of the third oxidation zone gas reaching said upper portion; and

introducing third reaction zone off-gas into

said second reaction mixture in said oxidation zone as at least part of the oxygen-bearing gas admixed with said second reaction mixture in said second oxidation zone.

4. A process according to claim 3 in which the oxygen-bearing gas admixed with said third reaction mixture in said third oxidation zone comprises air.

5. A process according to claim 3 or 4 in which the oxygen-bearing gas admixed with the third reaction mixture in said third oxidation zone is admixed at a rate selected to establish and maintain oxygen in said second reaction mixture in said second oxidation zone in stoichiometric excess relative to said hydrocarbon in said second reaction mixture in said second oxidation zone.

6. A process according to claim 5 in which the oxygen-bearing gas admixed with said second reaction mixture in said second oxidation zone comprises air.

7. A process according to any one of claims 3 to 6, in which aqueous solution of alkali is introduced into said second and third reaction mixtures in said second and third reaction zones.

8. A process according to any one of the preceding claims, in which the first reaction zone is above the second reaction zone, the second reaction zone is above the third reaction zone and the respective zones are separated from each other by gas permeable means.

9. A process according to any one of the preceding claims, in which the hydrocarbon is cumene, a m- or p-cymene, and  $\alpha$ - or  $\beta$ -

isopropylnaphthalene, a m- or p-diisopropylbenzene, 2-butylbenzene, or 2-pentylbenzene.

10. A process according to any one of the preceding claims, in which the hydrocarbon is cumene.

11. A process according to claim 10 in which the alkali is sodium carbonate and the concentration of the sodium carbonate in the aqueous solution is 1% by weight.

12. A process according to claim 11 in which the hydroperoxide concentration in the first reaction zone oxidate is 6—10% by weight, the hydroperoxide concentration in the second reaction zone oxidate is 13—17% by weight, and the concentration of the hydroperoxide in the third reaction zone oxidate is 20—30% by weight.

13. A continuous process for oxidizing secondary  $C_6$ — $C_7$  alkyl substituted aromatic hydrocarbons to the corresponding aralkyl hydroperoxide substantially as described herein with reference to the accompanying drawing.

14. A continuous process for oxidizing secondary  $C_6$ — $C_7$  alkyl substituted aromatic hydrocarbons to the corresponding aralkyl hydroperoxide substantially as described herein with reference to the example as set forth in the table.

15. An aralkyl hydroperoxide whenever prepared by the process of any one of the preceding claims.

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COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of  
the Original on a reduced scale

